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(54) METHOD OF LUBRICATING 2-STROKE ENGINES

(71) We, INSTITUT FRANCAIS DU PETROLE, formerly Institut Francais du Petrole des Carburants et Lubrifiants, a body corporate, organised and existing under the laws of France, of 4 avenue de Bois-Préau, 92 502 Rueil-Malmaison, Hauts-de-Seine, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention concerns the lubrication of 2-stroke engines.

It is known that 2-stroke engines may, according to their type, be lubricated either by a lubricant blended with the petrol used to operate them or by a lubricant that is not blended with the petrol but is dispensed by a pump and entrained by the air-petrol mixture fed to the engines. In this latter case, the bearings of the engine may be greased either by the lubricant thus introduced into the engine or by lubricant carried in an independent circuit provided exclusively for this purpose. In all of these cases, the lubricant finally passes into the combustion chamber and the products of its combustion are evacuated via an exhaust.

It is also known that the properties of the lubricants conventionally used in the lubrication of 2-stroke engines, particularly their action against seizure of the piston(s) and bearings and against seizure of the piston(s) in the cylinder(s), are such that, to ensure satisfactory functional reliability, it is necessary to use the lubricants in relatively large proportions, often more than 5% by weight and always at least 2% by weight, with respect to the fuel.

The use of such proportions of lubricant, which are far greater than those used in 4-stroke engines, has the following disadvantages: large quantities of partly or completely cracked lubricant are discharged through the exhaust; and only poor combustion of the lubricant-fuel mixture occurs with the consequent emission of large quantities of opaque fumes.

These disadvantages result in particularly harmful pollution either of the air or, in the case of outboard 2-stroke engines attached to boats, of water.

Another drawback resides in the formation of deposits in the combustion chamber and exhaust system, which results in losses of engine power and necessitates the frequent dismantling of the engine.

It has now been discovered that when certain polyesters are used as lubricants in 2-stroke engines they have superior lubrication properties with respect to known lubricants, particularly against seizure and jamming, and can therefore be used in far smaller quantities, with the result that the aforesaid disadvantages may be substantially reduced. Moreover, since these polyesters also have excellent anti-wear properties, their use, in smaller quantities than known lubricants, does not lead to increased engine-wear.

Accordingly, the invention provides a method of lubricating a 2-stroke engine, fed with a conventional fuel, that comprises introducing into said engine a lubricating composition comprising at least one polyester having one of the following formulae:

$$X\text{-}(\text{-}O\text{—}G\text{—}OOC\text{—}A\text{—}CO\text{-})_n\text{—}O\text{—}G\text{—}OOC\text{—}A\text{—}CO\text{—}Y$$

$$X\text{-}(\text{-}O\text{—}G\text{—}OOC\text{—}A\text{—}CO\text{-})_n\,O\text{—}G\text{—}O\text{—}\ X$$

$$Y\text{—}OC\text{—}A\text{—}CO\text{-}(\text{-}O\text{—}G\text{—}OOC\text{—}A\text{—}CO\text{-})_n Y$$

[*Price 33p*]

in which each of G is a residue of an aliphatic diol, each of A is a residue of a dicarboxylic acid selected from saturated and unsaturated aliphatic, halogenated saturated and unsaturated alicyclic and halogenated aromatic dicarboxylic acids, or a residue of a saturated or unsaturated aliphatic tricarboxylic acid, each of X is a hydrogen atom or an acyl radical derived from a monocarboxylic acid, each of Y is a hydroxyl group, a hydrocarbyloxy group derived from a primary or secondary monoalcohol, or a residue of a primary or secondary monoamine and n is an integer of at least 1.

G preferably contains from 2 to 22 carbon atoms. When any of A are residues of saturated or unsaturated aliphatic dicarboxylic acids, these residues preferably each comprise a straight-chain C_{2-18} hydrocarbon radical, as a main chain, and, optionally, at least one C_{1-30} hydrocarbon radical, as side chain(s). The monocarboxylic acid from which X may be derived generally has the formula

R—COOH

where R is a straight or branched chain aliphatic or alicyclic or aromatic radical for example comprising from 1 to 30, preferably from 8 to 18, carbon atoms.

The alcohols and amines from which Y may be derived generally have the formula RCH_2OH, R_2CHOH, RNH_2 or R_2NH, where R is as defined above. n indicates the degree of polycondensation of the polyester and is preferably from 1 to 10.

The polyesters used in the compositions of the invention are derived from one or more dicarboxylic acids selected from saturated and unsaturated aliphatic, halogenated saturated or unsaturated alicyclic and halogenated aromatic dicarboxylic acids and/or from one or more saturated or unsaturated aliphatic tricarboxylic acids, and from one or more aliphatic diols; they may or may not be blocked by primary or secondary monoamines, monohydric alcohols or monocarboxylic acids as appropriate.

The polyesters may be prepared in any known manner, for example by direct esterification from the appropriate polycarboxylic acid(s) and diol(s), preferably in the presence of an esterification catalyst, for example p-toluene sulphonic acid or zinc chloride; they may likewise be obtained by reaction of the appropriate diol(s) with (a) derivative(s) of the appropriate polycarboxylic acid(s) for example ester(s), chloride(s) or anhydride(s).

The reaction may be carried out by fusion of the reagents or in solution in an inert solvent, for example benzene, toluene or a xylene.

When a primary or secondary amine, monohydric alcohol or monocarboxylic acid is used as a blocking compound it may be introduced into the reaction medium either at the commencement of the reaction or after condensation of the polycarboxylic compound(s) with the diol(s).

Examples of aliphatic dicarboxylic acids that may be used in the preparation of the polyesters are tetrapropenylsuccinic acid, 2,2,4-trimethyl adipic acid, sebacic (decanedioic) acid, dodecanedioic acid, 2-octyl-1,11-undecanedioic acid and 2 - nonyl - 1,10-decanedioic acid and "dimers" obtained by dimerisation of unsaturated fatty acids such as oleic, linoleic and linolenic acids and possibly saturated by hydrogenation and/or halogenation.

Examples of halogenated alicyclic and aromatic dicarboxylic acids that may be used are 1,4,5,6,7,7 - hexachloro - (2,2,1)bicyclo-5 - heptene - 2,3 - dicarboxylic acid and tetrachlorophthalic acid.

Examples of aliphatic diols that may be used are ethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, eicosanediol, ethyl - 1,3 - hexanediol, 2,2,4-(and 2,4,4 -) trimethyl - 1,6 - hexanediol, 2,2 - dimethyl - 1,3 - propanediol, 2 - octyl-1,11 - undecanediol, and 2 - nonyl - 1,10-decanediol.

Examples of monocarboxylic blocking acids that may be used are acetic, propionic, butyric, pelargonic, 2 - ethyl - hexanoic, dodecanoic, stearic and isostearic acids and branched acids obtained by oxo synthesis from olefins, for example 2,2 - dimethyl - 1 - propanoic acid ("5-versatic acid") and "9,11-versatic acid".

Examples of blocking monohydric alcohols that may be used are methyl, ethyl, propyl, butyl, octyl, dodecyl, ketyl, octadecyl, 2-ethylhexyl and 3,5,5-trimethylhexyl alcohols, cyclohexanol, 2 - methylcyclohexanol and branched alcohols derived from branched monocarboxylic acids formed by oxo synthesis from olefins, for example benzyl alcohol and the monoalkyl glycol ethers.

Examples of blocking monoamines that may be used are methyl, dimethyl, ethyl, isopropyl, butyl, isobutyl, 2-ethylhexyl, cyclohexyl and methylcyclohexyl amines.

Examples of aliphatic tricarboxylic acids that may be used are the "trimeric" acids obtained by trimerisation of unsaturated fatty acids such as oleic, linoleic and linolenic acids and possibly saturated by hydrogenation and/or halogenation. When one or more aliphatic tricarboxylic acids is used, the carboxyl group present in A may be blocked by a primary or secondary monoamine or by a monohydric alcohol in the manner described above.

The lubricating composition may consist solely of one or more of the polyesters. Alternatively, it may also comprise, for example by way of diluent, one or more compositions such as light petroleum fractions, e.g. white spirit, kerosene or a jet fuel, for

example in proportions ranging up to 50% by weight, or the polyester(s) may be mixed in varying proportions with one or more known lubricants, for example mineral, paraffin and naphthene oils (refined for example with a solvent or hydrorefined) and synthetic lubricating oils obtained for example by oligomerization or polymerization of olefinic hydrocarbons and, possibly, subsequent hydrogenation (for example, in the case of polyisobutenes) of the resulting product.

In certain cases, the proportion of polyester(s) to known lubricant(s) may be very low, for example as low as 0.01% by weight; the polyester(s) then play(s) a simple role of anti-friction additive.

The polyesters may also be used blended with simple esters of ordinary alcohols (monoalcohols or polyols), for example isodecyl adipate, trimethylhexyl azelate or trimethylolpropane caprylate, simple esters of alkyleneglycol oligomers, for example dipropyleneglycol adipate or pelargonate, or complex esters.

In the method of the invention, the lubricating composition may comprise at least one additive that is used or described in the literature for incorporation into lubricating compositions for 2-stroke engines. Conveniently, a detergent additive, for example a detergent dispersing additive that leaves no residue is added, for example in a proportion of from 0.05 to 30%, preferably 5 to 20%, by weight of the composition, together with an anti-oxidising additive, for example phenol or an amine additive, for example in a proportion of from 0.1 to 10% by weight of the composition.

Whatever the composition of the lubricant, it has been observed that the presence therein of one or more organic compounds comprising at least one aliphatic chain containing from 8 to 24, advantageously from 10 to 18 and preferably 12, carbon atoms may be beneficial and in particular may enhance the seizure-resistant properties of the lubricating composition. These organic compounds may be of various types, for example carboxylic acids, simple esters, alcohols, amines, amides, amine salts or nitriles. Examples of such compounds are:

octanoic acid, decanoic acid, tetradecanoic acid, hexadecanoic acid, octadecanoic acid, octadecene-9-oic acid, and their lower alkyl esters, for example their methyl, ethyl, isopropyl, butyl, isobutyl and ethylhexyl esters, and natural fractions comprising mixtures of acids from octanoic acid up to hexadecanoic acid with a predominance of dodecanoic acid;

octanol, decanol, tetradecanol, hexadecanol, octadecanol, and fractions of straight-chain alcohols obtained by reduction of corresponding monocarboxylic acid fractions or by synthesis, for example polymerization of ethylene in the presence of an alkylaluminium compound followed by oxidation;

dodecanoic acid, lower alkyl dodecanoates, dodecanol and dodecylamine; and di- and tricarboxylic acids, obtained by dimerisation or trimerisation of monocarboxylic acids such as octadecene-9-oic or oleic, octadecadiene-9,10-oic or linoleic and octadecatriene-9,12,15-oic or linolenic acids, optionally followed by hydrogenation, and their C_1—C_6 alkyl esters.

The said organic compounds may, for example, be added in amounts of from 0.1 to 40%, preferably from 2.5 to 10%, by weight of the lubricating composition. According to the invention there can be used a fuel-lubricant mixture for 2-stroke engines that comprises from 0.05 to 10%, for example from 0.05 to 5%, preferably from 0.1 to 1%, of a lubricating composition according to the invention in a fuel that is used or described in the literature for use in 2-stroke engines and is advantageously a special fuel containing no lead.

The method of the invention may be used for lubricating separate-lubrication 2-stroke engines or for lubricating 2-stroke engines intended to be lubricated by a lubricant blended with the fuel. The method is applicable to land or marine engines cooled by air or by the circulation of water.

The following Examples illustrate the invention.

EXAMPLE 1.

The polyesters listed below were prepared by a method similar to that described in Belgian Patent Number 772,208.

Product A: A polyester formed from 164 g of a mixture of 2 - octyl - 1,11 - undecanedioic and 2 - nonyl - 1,10 - decanedioic acid isomers, 104 g of 2,2 - dimethyl - 1,3-propanediol and 200 g of dodecanoic acid and having a viscosity of 13.8 cSt at 98.9° C.

Product B: A polyester formed from 328 g of a mixture of 2 - octyl - 1,11 - undecanedioic and 2 - nonyl - 1,10 - decanedioic acid isomers and 115 g of 2,2 - dimethyl - 1,3-propanediol and having an acid index of 53.6, a hydroxyl index of 33 and a viscosity at 98.9° C. of 109 cSt.

Product C: A polyester formed from 230 g of dodecanedioic acid, 260 g of 2,2 - dimethyl-1,3 - propanediol and 50 g of dodecanoic acid and having an acid index of 1, a hydroxyl index of 11.7 and a viscosity at 98.9° C. of 248 cSt.

Product D: A polyester formed from 328 g of a mixture of 2 - octyl - 1,11 - undecanedioic and 2 - nonyl - 1,10 - decanedioic acid isomers, 194.5 g of 1,4,5,6,7,7 - hexachloro-(2,2,1)bicyclo - 5 - heptene - 2,3 - dicarboxylic acid, 312 g of 2,2 - dimethyl - 1,3-propanediol and 660 g of dodecanoic acid and having a viscosity at 98.9° C. of 14 cSt.

Product E: A polyester of "dimeric" acid (mixture of dicarboxylic acids resulting from dimerisation of a mixture of oleic, linoleic and linolenic acids) and 2,2 - dimethyl - 1,3-propanediol and having a viscosity at 98.9° C. of 2840 cSt.

Product F: A polyester of "dimeric" acid and 2,2 - dimethyl - 1,3 - propanediol having a viscosity at 98.9° C. of 1200 cSt.

Using the polyesters the lubricating compositions indicated in Table I below were prepared:

TABLE I

Lubricating composition	Composition by weight (%) Constituent 1		Constituent 2		Viscosity 98.9°C (cSt)	37.8°C (cSt)	VI_E
I	Product A	100	—	—	13.8	—	—
II	Product B	100	—	—	109	—	—
III	Product C	100	—	—	248	—	—
IV	Product D	100	—	—	14	—	—
V	Product E	20	Isodecyl adipate	80	9.9	55.5	179
VI	Product E	18	Trimethyl hexyl azelate	82	10.2	54.5	189
VII	Product F	8	Polyisobutene*	92	13	—	—

* Polyisobutene having molecular weight of 320.

The lubricating compositions set out in Table I were tested in admixture with an ordinary leadless petrol with a Research octane index of 94 in a Motobecane type AV7L 2-stroke engine. To estimate the seizure resistance properties of the mixture, the rise in temperature of the spark plug seal caused by a 400 r.p.m. fall in engine speed due to seizure of the piston in the cylinder which occured when cooling of the engine was discontinued, was measured. The higher the rise in temperature which it allowed, the better was the lubricant. The results are given in Table II below.

For comparison, similar tests were carried out using either polyisobutene alone in identical petrol, or a mineral oil in identical petrol the proportion of mineral oil in the mixture being 5.7% in accordance with known recommendations.

TABLE II

Lubricating Composition	% weight in the mixture	Rise in temperature (°C)
I	2	60
	1	60
	0.5	53
II	1	70
III	0.25	89
	0.1	86
	0.05	71
IV	1	59
V	1	60
VI	1	61
VII	1	63
Polyisobutene*	1	38
Mineral oils		
200 Neutral Solvent	5.7	42
400 Neutral Solvent	5.7	45
600 Neutral Solvent	5.7	51
Bright Stock Solvent	5.7	57

* Polyisobutene having molecular weight of 320.

EXAMPLE 2.

The lubricating compositions set out in Table III below were prepared. These lubricating compositions were tested by the method described in Example 1. The results are given in Table III.

TABLE III

Lubricating composition	Composition by weight (%) Constituent 1		Constituent 2		% weight in the fuel	Rise in temperature °C
VIII	Lubricant II	90	Dodecanoic acid	10	1	74
IX	Lubricant II	90	Methyl dodecanoate	10	1	76
X	Lubricant II	90	Dodecylamine	10	1	73

EXAMPLE 3.

Carbon deposit test

A lubricating composition (Lubricant XI) was prepared containing 80% by weight of Product A of Example 1 and 20% by weight of a multifunctional ashless additive "Oloa 340 D". From the seizure test results obtained in Example 1, it would be expected that if lubricant XI were used in fuel in an amount such that the fuel contained 0.5% by weight of Product A it would ensure a resistance against seizure at least equivalent to that of a 5% mixture of a commercial oil in the same fuel. Tests were conducted to determine whether the expected results were obtained. The fuel used for preparing the mixtures to be tested was a leadless petrol of Research octane index of 94.

The carbon deposit test carried out according to the method CEC 1.402.T.68 on an

engine of the MOTOBECANE Type AV7L lasted 100 hours and comprised various phases of operation, including an idle running period. It represented actual service of far longer duration.

The results are set out in Table IV below.

TABLE IV

	Commercial oil	Lubricant XI
Obstruction of the silencer, %	36.6	20.6
Obstruction of the exhaust port, %	10	0
Drop in power as a % of the value at the start of the test	0	0
Sparking plug incidents	0	0
Inspection of the piston: (merit/10):		
Freedom of the rings:		
1st ring	0	10
2nd ring	0	10
Varnish on the piston skirt	7.1	9.8
Carbon deposit in the grooves:		
1st groove	0	9.8
2nd groove	0	10
Varnish in the grooves:		
1st groove	0	9.0
2nd groove	0	10
Varnish in the bottom of the piston	2	10
Varnish on the inside wall of the piston	9.6	10
Carbon deposit on the crown	6.2	7.1
Scratching of the crown	8.2	9.5
Varnish on the rim of the piston	0	10
Varnish on the walls of the cylinder	7.3	10

It was observed that use of Lubricant XI in place of the commercial oil led to an improvement in the cleanliness of the engine, a considerable reduction in atmospheric pollution by the oil discharged at the exhaust and the almost complete absence of visible smoke.

WHAT WE CLAIM IS:—

1. A method of lubricating a 2-stroke engine, fed with a conventional fuel, that comprises introducing into said engine a lubricating composition comprising at least one polyester having one of the following formulae:

$$X\text{-}(\text{-O—G—OOC—A—CO-})_n\text{—O—G—OOC—A—CO—Y}$$

$$X\text{-}(\text{-O—G—OOC—A—CO-})_n\text{ O—G—O— X}$$

$$Y\text{—OC—A—CO-}(\text{-O—G—OOC—A—CO- })_n Y$$

in which each of G is a residue of an aliphatic diol, each of A is a residue of a dicarboxylic acid selected from saturated and unsaturated aliphatic, halogenated saturated, and unsaturated alicyclic and halogenated aromatic dicarboxylic acids, or a residue of a saturated or unsaturated aliphatic tricarboxylic acid, each of X is a hydrogen atom or an acyl radical derived from a monocarboxylic acid, each of Y is a hydroxyl group, a hydrocarbyloxy group derived from a primary or secondary monohydric alcohol, or a residue of a primary or secondary monoamine and n is an integer of at least 1.

2. A method according to claim 1, in which each of G contains from 2 to 22 carbon atoms, at least some of A are aliphatic radicals each comprising a straight-chain C_{2-18} hydrocarbon radical, and n is from 1 to 10.

3. A method according to claim 1, in which each of G contains from 2 to 22 carbon atoms, at least some of A are aliphatic radicals each comprising a straight-chain C_{2-18} hydrocarbon radical as a main chain and at least one C_{1-30} hydrocarbon radical as side chain(s), and n is from 1 to 10.

4. A method according to claim 2 or 3, in which at least some of A are derived from one or more saturated aliphatic dicarboxylic acids.

5. A method according to claim 2 or 3, in which at least some of A are derived from one or more unsaturated aliphatic dicarboxylic acids.

6. A method according to any preceding claim, in which, in addition to the polyester(s), the lubricating composition comprises one or more mineral oils and/or one or more synthetic lubricants.

7. A method according to any one of claims 1 to 5, in which the lubricating composition comprises at least one diluent for the polyester(s).

8. A method according to any one of claims 1 to 6, in which the lubricating composition comprises at least one simple ester.

9. A method according to any one of claims 1 to 5, in which the lubricating composition consists essentially of the polyester(s).

10. A method according to any one of claims 1 to 5, in which the lubricating composition comprises at least one organic compound comprising at least one C_{8-24} aliphatic chain and having one carboxylic acid, ester, alcohol, amine, amide, amine salt or nitrile function or consisting of a di- or tri-carboxylic acid obtained by dimerisation or trimerisation of a C_{18} unsaturated monocarboxylic acid optionally followed by hydrogenation, or a C_1—C_6 alkyl ester thereof.

11. A method according to claim 10, in which the said organic compound comprises a C_{12} aliphatic chain.

12. A method according to claim 10 or 11, in which the said organic compound represents from 0.1 to 40% of the weight of the lubricating composition.

13. A method according to any preceding claim, in which each of A is a residue of a dicarboxylic acid selected from saturated and unsaturated aliphatic, halogenated saturated and unsaturated alicyclic and halogenated aromatic dicarboxylic acids.

14. A method of lubricating a 2-stroke engine lubricated by a lubricant blended with the fuel, in which said engine is fed with a fuel-lubricant mixture that comprises a conventional fuel and from 0.05 to 10% by weight of a lubricating composition as described in any one of claims 1 to 9.

15. A method of lubricating a 2-stroke engine lubricated by a lubricant blended with the fuel, in which said engine is fed with a fuel-lubricant mixture that comprises a conventional fuel and from 0.05 to 10% by weight of a lubricating composition as described in any one of claims 10 to 12.

16. A method according to claim 14 or 15, in which the fuel-lubricant mixture comprises 0.05 to 5% by weight of said lubricating composition.

17. A method according to claim 1, in which a lubricating composition is used substantially as described in Example 1 or 3.

18. A method according to claim 1, in which a lubricating composition is used substantially as described in Example 2.

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